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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Work accomplished under contract N00014-81-K-0759 is summarized, and all technical reports and publications produced are summarized. References: 1. 2. 3. 4. 5. 6. 7. 8. 9. 10. 11. 12. 13. 14. 15. 16. 17. 18. 19. 20. 21. 22. 23. 24. 25. 26. 27. 28. 29. 30. 31. 32. 33. 34. 35. 36. 37. 38. 39. 40. 41. 42. 43. 44. 45. 46. 47. 48. 49. 50. 51. 52. 53. 54. 55. 56. 57. 58. 59. 60. 61. 62. 63. 64. 65. 66. 67. 68. 69. 70. 71. 72. 73. 74. 75. 76. 77. 78. 79. 80. 81. 82. 83. 84. 85. 86. 87. 88. 89. 90. 91. 92. 93. 94. 95. 96. 97. 98. 99. 100. 101. 102. 103. 104. 105. 106. 107. 108. 109. 110. 111. 112. 113. 114. 115. 116. 117. 118. 119. 120. 121. 122. 123. 124. 125. 126. 127. 128. 129. 130. 131. 132. 133. 134. 135. 136. 137. 138. 139. 140. 141. 142. 143. 144. 145. 146. 147. 148. 149. 150. 151. 152. 153. 154. 155. 156. 157. 158. 159. 160. 161. 162. 163. 164. 165. 166. 167. 168. 169. 170. 171. 172. 173. 174. 175. 176. 177. 178. 179. 180. 181. 182. 183. 184. 185. 186. 187. 188. 189. 190. 191. 192. 193. 194. 195. 196. 197. 198. 199. 200. 201. 202. 203. 204. 205. 206. 207. 208. 209. 210. 211. 212. 213. 214. 215. 216. 217. 218. 219. 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OFFICE OF NAVAL RESEARCH

Final Technical Report
on Contract N00014-81-k 0759

Period covered: 1 July 1981 - 30 September 1987

A. Summary of Work Accomplished

A new second-quantization representation was derived for low-energy positron-hydrogen scattering. This work, which was published in Phys. Rev. A 26, 217 (1982) and released as Technical Report QFT-2 of this contract, served as the foundation for our subsequent calculation of differential cross sections for the positronium formation reaction $e^+ + H \rightarrow Ps + H^+$. The applicability of our representation for positron-hydrogen scattering to the above-mentioned reactive process stems from the fact that our novel second-quantization representation treats all channels (both scattering and reactive) on an equal footing. The calculations for the positronium-formation reaction, carried out by the P.I. and his colleague Prof. Edgardo Ficocelli Varracchio, were published in J. Phys. B 16, 1097 (1983) and released as Technical Report QFT-3 of this project. During his visit at the university of Oregon for the purpose of this research collaboration, Prof. Ficocelli Varracchio also wrote a review on the field-theoretic approach to the theory of three-body atomic collision phenomena based on our novel second quantization representation. This was published in Ann. Phys. (N.Y.) 145, 131 (1983) and released as Technical Report QFT-4 of this contract. The same general approach was used by the P.I. and his Postdoctoral Research Associate Dr. J.D. Gilbert to derive the Fock-Tani representation Hamiltonian for electron-hydrogen scattering. This was released as Technical Report QFT-5.

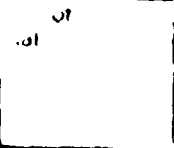
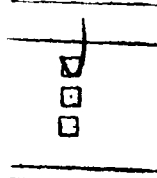
As a basis for generalization of our calculations on atomic collision phenomena so as to include perturbing effects of the environment (for example, a plasma) in which the colliding atoms and ions are immersed, the P.I. and his Postdoctoral Research Associate Dr. Charles F. Hart developed a general technique of "Liouwellian Green's functions" for calculation of dissipative energy-shift and line-broadening effects on atoms in a perturbing medium. This research was published as a series of three papers: Phys. Rev. A 28, 1056 (1983), Phys. Rev. A 28, 1072 (1983), and Phys. Rev. A 28, 186 (1983) and released as Technical Reports QFT-6, QFT-7, and QFT-8 of this contract. An abbreviated account of this work was also published in the volume Spectral Line Shapes, Vol. 2 (Walter de Gruyter, Berlin, 1983) which constitutes the proceedings of an International Conference on Spectral Line Shapes at which the P.I. described this work.

In the course of investigating the theory of the charge-exchange reaction $D^+ + H \rightarrow D + H^+$, the P.I. discovered a technique for elimination of the coordinates of any one of a system of N interacting particles by performing a canonical transformation to an accelerated coordinate system centered on that particle. This was published in Phys. Rev. A 28, 3635 (1983) and released as Technical Report QFT-9.

Realizing that a truly fundamental treatment of the theory of atomic and ionic collisions occurring in a perturbing medium must come to grips with the problem of how to define and calculate the perturbed bound wave functions of the colliding species, the P.I. and his Postdoctoral Research Associate Dr. Charles F. Hart derived a new variational principle for determination of such perturbed, decaying (finite lifetime) states. This was published in Phys. Rev. Lett. 51, 1725 (1983) and released as Technical Report QFT-10. This was also published in abbreviated form in Quantum Electrodynamics and Quantum Optics, ed. A.O. Barut (Proceedings, NATO



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Advanced Study Institute, Boulder, Colorado, 1983; Plenum, New York, 1984), pp. 323ff., at which conference the P.I. was an invited speaker.

Building on our previous calculations for the positronium formation reaction and our subsequent work on similar three body problems, the P.I., his Postdoctoral Research Associates Dr. P.C. Ojha and Dr. J.D. Gilbert, and his Ph.D. dissertation student Jack C. Straton formulated an improved first-order theory of the charge transfer reaction $H^+ + H(1s) \rightarrow H(1s) + H^+$ and used it to calculate differential and total cross sections for this reaction. The results were found to be much more accurate than the conventional first Born approximation and to give very good agreement with experiment for the total cross section at energies greater than 10 keV and for the differential cross section at energies 25, 60, and 125 keV in an angular range of ~ 1 mrad about the forward direction. This work was published in Phys. Rev. A 33, 112 (1986) and released as Technical Report QFT-11. The first-order approach was subsequently extended by the P.I. to a formulation of the distorted-wave method in this representation. It was published in Phys. Rev. A 33, 905 (1986) and released as Technical Report QFT-12.

The P.I. was awarded a (unsolicited) Humboldt Prize (U.S. Senior Scientist Award) by the Alexander von Humboldt Stiftung for the period 1984-85 and spent three three to four-month periods working in the Max Planck Institut fur Strahlenchemie, Mulheim/Ruhr, West Germany during the years 1984-86. These visits were funded entirely by the A.v.H. Stiftung and the Max Planck Society. Therefore the publications resulting from the research collaboration between the P.I. and his colleagues there do not appear as ONR Technical Reports. However, a few of these publications are closely related to the research program of this ONR contract and are therefore appended to the Index of Publications with a note that they were not funded by the ONR.

The P.I.'s Ph.D. dissertation student Jack C. Straton completed his Ph.D. dissertation, entitled "Charge transfer in a $3 \rightarrow 2$ -body, reduced mass Fock-Tani representation: first order results and an introduction to higher order effects", based on research funded by this ONR contract, and received his Ph.D. degree in June 1986. He is currently in the second year of an appointment as a National Research Council - NASA Postdoctoral Research Associate at the NASA Goddard Space Flight Center in Greenbelt, MD, where he works in the atomic theory group of A. Temkin, R.J. Drachman, and A.K. Bhatia. Prior to taking up his duties under that appointment, he completed two papers based on his research. These were published in Phys. Rev. A 35, 2729 (1987) and Phys. Rev. A 35, 3725 (1987) and released as Technical Reports QFT-13 and QFT-14.

In the course of generalizing our treatment of reactive collisions of atoms to include perturbing effects of the environment (for example, a plasma) we realized that the standard Lippmann-Schwinger theory of collisions does not apply to reactions involving metastable or unstable quasibound states, as occur, for example, in molecular predissociation, atomic autoionization, the Auger effect, and atomic recombination to highly perturbed and broadened atomic states in a plasma. A generalization of Lippmann-Schwinger collision theory applicable to such cases was worked out, published in Int. J. Quantum Chem. 29, 1483 (1986), and released as Technical Report QFT-15.

The calculations on atomic charge-transfer reactions thus far described were based on an improved first-order theory obtained by canonically transforming the Hamiltonian and then applying the first Born approximation in the new representation. One of the P.I.'s Ph.D. dissertation students, Chaomei Hu, has extended this approach so as to include an important class of second-Born contributions and performed calculations of improved differential cross-sections for charge exchange. Specifically, she included both initial and final-state elastic scattering contributions in a post-prior symmetrized Fock-Tani second Born calculation of differential cross sections for the charge-exchange reaction $H^+ + H \rightarrow H + H^+$. In addition she calculated post-prior symmetrized Fock-Tani first Born differential cross sections for the reactions $H^+ + H(1s) \rightarrow H(n\ell m) + H^+$ and $e^+ + H(1s) \rightarrow Ps(n\ell m) + H^+$ for the cases $n = 1$ and $n = 2$, $\ell = 0, 1$. Her Ph.D. dissertation will be completed this year and the ONR will be provided with copies of the dissertation and all resultant publications, with acknowledgement of the ONR support.

The P.I. and another of his Ph.D. dissertation students, Fernando A. Gutierrez, began a program of calculation of cross sections for those reactive processes of atoms in plasmas which are strongly influenced by the plasma environment. Specifically, we developed the theory of a new mechanism for atomic recombination to highly-excited and perturbed states of hydrogen in a plasma, whereby the binding energy is carried away by a plasmon (quantized collective plasma oscillation) rather than a photon (radiative recombination) or a third particle. This work has been submitted to Phys. Rev. A and a preprint is appended to this Report. Copies of the dissertation of Mr. Gutierrez (expected to be completed this year) and any resultant publications will be sent to the ONR, and ONR support of this work will be acknowledged. The approach generalizes our earlier work on reactive scattering by large systems cited as item 17 in the Index of Publications.

B. Index of Technical Reports

- QFT-2: "Fock-Tani representation for positron-hydrogen scattering"
- QFT-3: "Ideal-space treatment of the $e^+ + H \rightarrow Ps + H^+$ process"
- QFT-4: "Field theory of the $e^+ - H$ three-body system"
- QFT-5: "Fock-Tani representation for electron-hydrogen scattering"
- QFT-6: "Liouvillian Green's functions and self energies for energy-shift and decay phenomena"
- QFT-7: "Liouvillian Green's function theory of spectral line shape"
- QFT-8: "Improved Heisenberg equations-of-motion approach for nonequilibrium decay phenomena"
- QFT-9: "Reduction of a quantum n-body problem to an (n-1) - body problem"
- QFT-10: "New variational principle for decaying states"
- QFT-11: "Fock-Tani transformation and a first-order theory of charge transfer"
- QFT-12: "Distorted-wave amplitudes, distorted-wave Born approximation, and self-energies in the Fock-Tani theory of rearrangement collisions"
- QFT-13: "Fourier transform of the product of N one-center hydrogenic orbitals"
- QFT-14: "Reduced-mass Fock-Tani representations for $a^+ + (b^+c^-) \rightarrow (a^+c^-) + b^+$ "
- QFT-15: "Theory of half-collision cross sections"

C. Index of Publications

1. M.D. Girardeau, "Fock-Tani representation for positron-hydrogen scattering", Phys. Rev. A 26, 217 (1982).
2. E. Ficocelli Varracchio and M.D. Girardeau, "Ideal-space treatment of the $e^+ + H \rightarrow Ps + H^+$ process", J. Phys. B 16, 1097, (1983).
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13. Jack C. Straton, "Fourier transform of the product of N one-center hydrogenic orbitals", Phys. Rev. A 35, 2729 (1987).
14. Jack C. Straton, "Reduced-mass Fock-Tani representations for $a^+(b^+c^-) \rightarrow (a^+c^-) + b^+$ and first-order results for $\{abc\} = \{ppe, epe, \mu p \mu, \mu d \mu, \text{ and } \mu t \mu\}$ ", Phys. Rev. A 35, 3725 (1987).
15. M.D. Girardeau, "Theory of half-collision cross sections", Int. J. Quantum Chem. 29, 1483 (1986).
16. M.D. Girardeau and F.A. Gutierrez, "Collective mechanism for atomic recombination in plasmas", Phys. Rev. A (submitted January 1988).

Not supported by this ONR contract but closely related to the supported program:

17. M.D. Girardeau and C.I. Ivanov, "Space-time correlation function representation of reactive scattering by large systems", Chem. Phys. Lett. 131, 389 (1986).
18. H. Kupka, M.D. Girardeau, C.I. Ivanov, and O.E. Polansky, "Vibrational and rotational energy distribution of photofragmentation products in electronic predissociation processes. I.", submitted to J. Chem. Phys.
19. H. Kupka, U. Becker, and M.D. Girardeau, "... II", submitted to J. Chem. Phys.

APPENDIX: Work on plasmon-mediated atomic recombination
in progress at termination of the contract

Collective mechanism for atomic recombination in plasmas

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Abstract

A new mechanism is proposed for atomic recombination in plasmas, whereby the binding energy is carried away by a plasmon. It is suggested that this mechanism may compete with radiative and three-body modes in the case of recombination to sufficiently highly-excited and perturbed states of hydrogen. A procedure for calculation of the transition rate is outlined in a model which treats the plasma oscillations by the Bohm-Pines canonical transformation and the atomic bound states by a second canonical transformation.

Two fundamental quantities in a classical plasma are the Debye screening length $\lambda_D = (k_B T / 8\pi n e^2)^{1/2}$ and the (longitudinal) plasma frequency¹

$$\omega_q \approx \omega_p \left(1 + \frac{3}{2} \lambda_D^2 q^2 \right) , \quad \lambda_D q < 1 \quad (1)$$

where $\omega_p = (4\pi n e^2 / m)^{1/2}$. The first term in (1) arises from the long-range correlations between electrons and the second from their thermal motion. We consider herein only the simplest, one-component model; accordingly, e and m are the electron charge and mass. Quantization gives rise to plasmons, the longitudinal analog of the usual (transverse) photons, with energies $\sim 4 \times 10^{-11} n^{1/2}$ eV where n , the electron number density, is in cm^{-3} .

In analogy with the case of Cherenkov photon emission, the condition for conservation of energy and momentum in the emission of a real plasmon of momentum $\hbar \vec{q}$ and energy $\hbar \omega_q$ by an electron of velocity \vec{v} is² $\omega_q = \vec{q} \cdot \vec{v}$. Since there is a maximum plasmon wave vector^{1,3} $q_c \sim \lambda_D^{-1}$, there is a critical velocity $v_c \sim \omega_p \lambda_D$ below which real plasmon emission cannot occur. The purpose of this note is to suggest and briefly analyze a new collective mechanism for atomic recombination in plasmas, whereby the binding energy is carried away by a plasmon rather than a photon or a third particle. A semiclassical picture of the process is shown in Fig. 1. An electron in an unbound (hyperbolic) orbit with respect to the given proton approaches it with a small enough impact parameter that the speed of the electron near perihelion exceeds

the critical velocity v_c mentioned above, leading to emission of a real plasmon and capture of the electron into an elliptic orbit.

Consider a hydrogen plasma with $n \sim 10^{18}/\text{cm}^3$ and $k_B T \sim 1$ eV ; then $\lambda_D \sim 100 a_0$ (a_0 = Bohr radius of the unperturbed hydrogen atom) and $\hbar\omega_p \sim 4 \times 10^{-2}$ eV. In zeroth approximation one may determine the perturbed hydrogen levels and wave functions by solution of the Schrödinger equation with the screened (Debye-Hückel) potential. One finds^{4,5} that the 8s level has binding energy $\sim 4 \times 10^{-2}$ eV and the 9h level (the highest screened Coulomb bound state for the given value of λ_D) $\sim 8 \times 10^{-3}$ eV . These binding energies are an order of magnitude smaller than those of the unperturbed states, so that plasmon-mediated recombination to these levels is energetically allowed.

A correct calculation of the recombination cross section requires a quantum-mechanical treatment of at least the electrons. We shall use a simplified model consisting of a single, fixed proton at the origin immersed in a medium composed of the electrons and a uniform, immobile positive background which crudely models the other protons ("jellium"). The interactions of the electrons with each other, with the one chosen proton, and with the rigid positive background gives rise to collective plasma modes which are crucial for this mechanism of recombination. The Hamiltonian \hat{H} in Bohm-Pines representation³ further transformed into Fock space is

$$\begin{aligned}
\hat{H} &= \hat{T}_e + \hat{H}_{pl} + \hat{V}_{e-e} + \hat{V}_{e-p} + \hat{V}_{e-pl} + \hat{V}_{p-pl} + N\Delta \\
\hat{T} &= \sum_k \left(\hbar^2 k^2 / 2m \right) \hat{e}_k^\dagger \hat{e}_k \\
\hat{H}_{pl} &= \sum_{q < q_c} \hbar \omega_q \left(\hat{c}_q^\dagger \hat{c}_q + \frac{1}{2} \right) \\
\hat{V}_{e-e} &= \frac{1}{2} \Omega^{-1} \sum_{q > q_c} \sum_{kk'} \left(4\pi e^2 / q^2 \right) \hat{e}_{k+q}^\dagger \hat{e}_{k'-q}^\dagger \hat{e}_{k'} \hat{e}_k \\
\hat{V}_{e-p} &= - \Omega^{-1} \sum_{q > q_c} \sum_k \left(4\pi e^2 / q^2 \right) \hat{e}_{k-q}^\dagger \hat{e}_k \\
\hat{V}_{e-pl} &= \Omega^{-1} \sum_{\substack{q < q_c \\ qkk', k' > q_c}} \left(\frac{4\pi e^2}{(k')^2} \right) \left(\frac{2\pi e^2 \hbar \omega_q}{\Omega} \right)^{1/2} (\hbar q)^{-1} \epsilon_{qkk'} \left(\hat{c}_q^\dagger \hat{e}_{k+k'-q}^\dagger \hat{e}_k + \text{h.c.} \right) \\
\hat{V}_{p-pl} &= - \sum_{q < q_c} \left(2\pi e^2 \hbar \omega_q / q^2 \Omega \right) \left(\hat{c}_q^\dagger + \hat{c}_q \right) \\
\Delta &= - \sum_{q < q_c} \left(2\pi e^2 / q^2 \Omega \right) = - \pi^{-1} e^2 q_c \quad (2)
\end{aligned}$$

Here \hat{e}_k and \hat{e}_k^\dagger annihilate and create electrons with momentum

$\hbar\vec{k}$, $\hat{c}_{\vec{q}}$ and $\hat{c}_{\vec{q}}^\dagger$ annihilate and create plasmons with momentum $\hbar\vec{q}$ and energy $\hbar\omega_{\vec{q}}$, q_c is a wave vector cutoff $\sim \lambda_D^{-1}$, Ω is the volume of the system (periodic boundary conditions), $N=n\Omega$ is the number of electrons, and

$$\epsilon_{\vec{q}\vec{k}\vec{k}'} = (\omega_{\vec{q}} - \hbar\vec{q}\cdot\vec{k}/m)^{-1} - [\omega_{\vec{q}} - (\hbar/m)\vec{q}\cdot(\vec{k} + \vec{k}')]^{-1} \quad (3)$$

In (3) we have neglected terms of order q^2 for $q < q_c$; these represent pure quantum effects and are very small (less than 1% of $\omega_{\vec{q}}$ for $n \sim 10^{18}$ and $kT \sim 1$ eV). In (2) \hat{T}_e represents the free electron kinetic energy, \hat{H}_{pl} the free plasmons, \hat{V}_{e-e} a screened electron-electron interaction and \hat{V}_{e-p} the corresponding screened electron-proton interaction, \hat{V}_{e-pl} the electron-plasmon interaction representing emission and absorption of single plasmons by electrons in the field of the proton, \hat{V}_{p-pl} the absorption and emission of virtual plasmons by the proton, and Δ a constant negative energy shift which results from the long-range correlations between the electrons⁶.

A few remarks are in order:

(a) If we had considered a proton at \vec{r}_0 with velocity $v_0 > v_c$, then \hat{V}_{p-pl} , containing a factor $\exp(-i\vec{q}\cdot\vec{r}_0)$, would describe Cherenkov-like emission of real plasmons by the fast proton. (In fact, this was the original motivation of Pines³). In the present case the proton is at rest and the proton emits and absorbs only virtual plasmons, which will be found to give a negative energy shift.

(b) In the original work of Pines³ \hat{V}_{e-pl} was neglected compared to the leading term giving real plasmon emission by the proton. In the present case, since \hat{V}_{p-pl} gives only a constant energy shift, \hat{V}_{e-pl} is the leading term for the dynamics of real plasmon emission by electrons in the field of the proton.

(c) In coordinate space \hat{V}_{e-p} can be represented to a good approximation^{3,7} by the potential

$$- \sum_i \left(e^2 / r_i \right) e^{-q_c r_i} \quad (4)$$

where r_i is the distance between the proton and the *i*th electron.

(d) The derivation of (2) and (3) is rather lengthy and is given in the Bohm-Pines papers and a forthcoming paper on the details of the plasmonic recombination mechanism.

The demonstration that \hat{V}_{p-pl} gives rise to a negative energy shift proceeds as in other Bose quasiparticle theories, by carrying out a canonical transformation to cancel the terms \hat{V}_{p-pl} linear in plasmon operators \hat{c}_q and \hat{c}_q^\dagger . The required (unitary) transformation is

$$\hat{S}^{-1} \hat{c}_q \hat{S} = \hat{c}_q + \left(2\pi e^2 / \Omega q^2 \hbar \omega_q \right)^{1/2}, \quad \hat{S}^{-1} \hat{c}_q^\dagger \hat{S} = (\hat{S}^{-1} \hat{c}_q \hat{S})^\dagger \quad (5)$$

and leads to a negative shift Δ identical with (2):

$$\hat{S}^{-1} (\hat{H}_{pl} + \hat{V}_{p-pl}) \hat{S} = \hat{H}_{pl} + \Delta \quad (6)$$

As in similar fixed-source theories, this shift is interpreted as the energy of virtual zero-point plasmons absorbed and emitted by the proton. The only other term in the Hamiltonian (2) affected by the transformation (5) is the term \hat{V}_{e-pl} which is transformed into $\hat{V}_{e-pl} + \hat{V}_{e-p}'$ where

$$\hat{V}_{e-p}' = n^{-2} (2\hbar)^{-1} \sum_{(q < q_c, k, k' > q_c)} \left(\frac{4\pi e^2}{q^2} \right) \left(\frac{4\pi e^2}{(k')^2} \right) (\epsilon_{qkk'} + \epsilon_{-q, k+k', -q, -k'}) \hat{e}_{k+k'}^\dagger - q \hat{e}_k \quad (7)$$

which can be regarded as a dynamical correction to the static screened Coulomb proton-electron interaction \hat{V}_{e-p} . Inserting the explicit expression (3), one sees that the summand tends to cancel between regions with opposite alignments of the relevant vectors, whereas $(4\pi e^2/q^2)$ in \hat{V}_{e-p} is isotropic. It is therefore within the spirit of the RPA to neglect \hat{V}_{e-p}' compared to \hat{V}_{e-p} , and we shall do so herein. Indeed, if one neglects \vec{q} compared to \vec{k}' (since $q < q_c$, $k' > q_c$) and neglects $(\hbar q^2/2m)$ compared to ω_q as was done in (3), then for fixed \vec{k} and \vec{k}' the summand is an odd function of \vec{q} , so that \hat{V}_{e-p}' vanishes in this approximation.

At this point it is interesting to compare our result with the Ecker-Weizel potential^{8,9}

$$V_{EW}(r) = -e^2 \left[(1/r) e^{-r/\lambda_D} + (1/\lambda_D) \right] \quad (8)$$

between electrons and protons in a plasma, which has been used to interpret the plasma shifts of the discrete and continuous spectra of hydrogen. If we use the Debye-Hückel potential for the screened interaction \hat{V}_{e-p} in coordinate space and add the negative shift 2Δ [one Δ from the proton energy shift, Eq. (6), and another Δ from the energy shift of each electron, Eqs. (1) and (2)] then we obtain an effective potential

$$V_{\text{eff}}(r) = -e^2 \left[(1/r)e^{-r/\lambda_D} + (0.7/\lambda_D) \right] \quad (9)$$

which is very similar to (8).

Another change of representation is useful for extracting from \hat{V}_{e-pl} the term representing free-bound electron transitions with plasmon emission. The required canonical transformation in the simplest case where the bound state is a single-particle state (the proton being treated here as a fixed force center) is effected by a unitary operator \hat{U} given by^{10,11}

$$\hat{U} = \exp \left(\frac{\pi}{2} \hat{F} \right) , \quad \hat{F} = \sum_{\nu} \left(\hat{A}_{\nu}^{\dagger} \hat{a}_{\nu} - \hat{a}_{\nu}^{\dagger} \hat{A}_{\nu} \right) \quad (10)$$

where \hat{A}_{ν} and \hat{A}_{ν}^{\dagger} are the (Fermi) annihilation and creation operators for electrons bound in (here perturbed) hydrogen orbitals centered on the proton at the origin:

$$\hat{A}_\nu^\dagger = \sum_k \tilde{\phi}_\nu(k) \hat{e}_k^\dagger, \quad \hat{A}_\nu = (\hat{A}_\nu^\dagger)^\dagger \quad (11)$$

The index ν stands for (nlm) (and the spin z -component s , which will be suppressed herein); $\tilde{\phi}_\nu$ is the (perturbed) hydrogen momentum wave function, the Fourier transform of the perturbed spatial wave function $\phi_\nu(x)$. The new bound state Fermi annihilation and creation operators \hat{a}_ν and \hat{a}_ν^\dagger introduced by this transformation anticommute with the original (plane-wave) electron operators \hat{e}_k and \hat{e}_k^\dagger (although the \hat{e}_k and \hat{A}_ν^\dagger do not anticommute) and they commute with the plasmon operators \hat{c}_q and \hat{c}_q^\dagger . The canonical transformation effected by (10) is

$$\hat{U}^{-1} \hat{e}_k \hat{U} = \hat{e}_k - \sum_{kk'} \Delta_{kk'} \hat{e}_{k'} + \sum_\nu \tilde{\phi}_\nu(k) \hat{a}_\nu \quad (12)$$

where $\Delta_{kk'}$ is the bound state kernel

$$\Delta_{kk'} = \sum_\nu \tilde{\phi}_\nu(k) \tilde{\phi}_\nu^*(k') \quad (13)$$

Insertion of (12) into \hat{V}_{e-pl} , Eq. (2), yields several terms; the one describing the plasmonic recombination and the inverse ionization process is

$$\hat{V}(e \rightleftharpoons a + pl) = \sum_{\substack{kq\nu \\ (q < q_c)}} \left(\hat{c}_q^\dagger \hat{a}_\nu^\dagger (q\nu | V | k) \hat{e}_k + \text{h.c.} \right) \quad (14)$$

with

$$\begin{aligned} (q\nu | V | k) = \Omega^{-3/2} \left(\frac{2\pi e^2 \hbar \omega_q}{q^2} \right)^{1/2} \sum_{k' > q_c} \left(\frac{4\pi e^2}{(k')^2} \right) \left[\tilde{\phi}_\nu^*(k+k'-q) \xi_{qkk'} \right. \\ \left. - \sum_{k''} \tilde{\phi}_\nu^*(k''+k'-q) \xi_{qk''k'} \Delta_{k'k} \right] \end{aligned} \quad (15)$$

The effect of the subtraction term involving $\Delta_{k',k}$ is to orthogonalize the k dependence of the matrix element to the bound electron subspace. This is physically correct since \hat{e}_k annihilates an unbound electron. An equivalent point of view is to regard \hat{e}_k as the annihilation operator for an orthogonalized plane wave rather than a (Born approximation) free plane wave.

The physics of the emission in the matrix element (15) is contained in $\xi_{qkk'}$. Interpreting $\vec{v}_k = \hbar \vec{k}/m$ as the random (classical) velocity of the electrons in the plasma, one sees that the first term in (3) has a singularity at $\omega_q = \vec{q} \cdot \vec{v}_k$. This is the previously-mentioned condition for real plasmon emission. Because of the constraint $q < q_c$ only the few electrons in the

high-velocity tail of the Maxwellian distribution will be able to satisfy this condition. For this reason Bohm and Gross¹ neglected the singularity in getting the dispersion relation (1); we continue using this approximation here. Things are different for the second term in (3), where the singularity occurs at

$$\omega_q = \vec{q} \cdot [\vec{v}_k + (n\vec{k}'/m)] \quad (16)$$

The term $n\vec{k}'/m$ represents the increase in velocity of the electrons produced by the short range ($k' > q_c$) attractive interaction with the proton; it is crucial for the mechanism in which we are interested, because now electrons with any velocity in the field of the proton are potentially able to produce real plasmon emission. The reason is that the sum on k' appearing in (15) ensures that for any \vec{v}_k there is always a \vec{k}' such that (16) is satisfied. This is consistent with the semiclassical picture of Fig. 1, according to which an electron starting with a low velocity \vec{v}_k can increase its velocity until it emits a plasmon and becomes bound to the proton.

In zeroth approximation the wave functions $\phi_\nu(k)$ in (15) can be taken to be the eigenstates of the screened Coulomb potential satisfying

$$\left(n^2 k^2 / 2m \right) \phi_\nu(\vec{k}) - n^{-1} \sum_{q > q_c} \left(4\pi e^2 / q^2 \right) \phi_\nu(\vec{k} + \vec{q}) = \epsilon_\nu \phi_\nu(\vec{k}) \quad (17)$$

With the above choice one neglects the imaginary part of the atomic self energy, i.e., the finite lifetime of the perturbed atomic state. In particular, the simplified model considered herein neglects the Stark broadening due to the other positive ions¹² since they are treated as a uniform background. The Stark broadening due to the electrons is in principle included if one uses the appropriate generalized Schrödinger equation¹³ and this broadening is expected to be comparable¹² to that due to the positive ions at the densities and temperatures considered herein ($n \sim 10^{18}/\text{cm}^3$, $k_B T \sim 1 \text{ eV}$). We intend to generalize the treatment to a two-component plasma (both protons and electrons treated dynamically) in subsequent work.

The leading approximation to the transition rate for plasmon-mediated recombination is

$$W(q\nu|k) = (2\pi/\hbar^2) |(q\nu|T|k)|^2 \langle \hat{N}_k (1 + \hat{N}_q) (1 - \hat{N}_\nu) \rangle \delta(\epsilon_{fi}) \quad (18)$$

where

$$\begin{aligned} \epsilon_{fi} &= \hbar\omega_q + \epsilon_\nu - (\hbar^2 k^2 / 2m) \\ \hat{N}_k &= \hat{e}_k^\dagger \hat{e}_k \\ \hat{N}_q &= \hat{c}_q^\dagger \hat{c}_q \\ \hat{N}_\nu &= \hat{a}_\nu^\dagger \hat{a}_\nu \end{aligned} \quad (19)$$

The expression (18) is the product of the standard expression for the transition rate of a reaction in vacuum by a statistical factor $\langle \dots \rangle$ expressing the effects of occupancy of the initial and final states. In thermal equilibrium

$$\langle \dots \rangle \approx \langle \hat{N}_k \rangle \left(1 + \langle \hat{N}_q \rangle \right) \left(1 - \langle \hat{N}_\nu \rangle \right) \quad (20)$$

This is the standard statistical factor for a transition in a medium. Since the model only allows formation of a single atom (only one proton at the origin, all others a "smeared background") and $\langle \hat{N}_\nu \rangle$ is the mean occupation of level ν before formation of an atom in this state, we may take $\langle \hat{N}_\nu \rangle = 0$ and replace the Fermi blocking factor $(1 - \langle \hat{N}_\nu \rangle)$ by unity. The mean number $\langle \hat{N}_q \rangle$ of plasmons at each given q is also $\ll 1$ in the density-temperature regime under consideration (nondegenerate plasmon gas). Then (18) reduces to

$$W(q\nu|k) \approx (2\pi/\hbar^2) |(q\nu|T|k)|^2 f_k \delta(\epsilon_{fi}) \quad (21)$$

where f_k is the electron distribution function $\langle \hat{N}_k \rangle$ of the plasma, nearly Maxwellian in the given regime. In leading order the T matrix $(q\nu|T|k)$ reduces to the Hamiltonian matrix element $(q\nu|V|k)$ for the given reaction. Although this has the appearance of a Born approximation, it is expected to be much better than the usual "bare Born" approximation. In the first place, the atomic wave function is the screened Coulomb one, which takes into account in zeroth order the strong perturbation due to the plasma environment. In the second place the matrix element (15) includes the orthogonalization correction which is neglected in the usual Born approximation. A similar orthogonalization term has been proposed previously as a correction to Born-

approximation photoionization matrix elements¹⁴. In the present formulation this term arises naturally as a consequence of the canonical transformation (12).

The numerical evaluation of the plasmonic recombination rate and a comparison with the radiative rate is underway; this together with a more detailed description of the representations used herein will be given in a subsequent publication. We also plan to generalize the theory to the more realistic two-component plasma case.

Acknowledgement

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Footnotes

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Figure Caption

Fig. 1. Semiclassical picture of recombination by plasmon emission. The wavy line denotes the plasmon and the dashed line the "post-collision" hyperbolic orbit which would have been followed had the plasmon not been emitted.

